

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 December 2000 (14.12.2000)

PCT

(10) International Publication Number
WO 00/75254 A1

(51) International Patent Classification⁷: C09J 5/08,
C08J 9/32, B60J 10/02, 10/00

(21) International Application Number: PCT/GB00/02059

(22) International Filing Date: 26 May 2000 (26.05.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
9912694.8 2 June 1999 (02.06.1999) GB

(71) Applicants and

(72) Inventors: BAIN, Peter, Stewart [GB/GB]; 103 Rein
Road, Wakefield WF3 1JQ (GB). MANFRE, Giovanni
[IT/IT]; Via Vicenza 11, I-37042 Caldiero (IT).

(74) Agent: HARRISON GODDARD FOOTE; Tower
House, Merrion Way, Leeds LS2 8PA (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE,
DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU,
ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS,
LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO,
NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR,
TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 00/75254 A1

(54) Title: ADHESIVE COMPOSITION COMPRISING THERMOEXPANDABLE MICROCAPSULES

(57) Abstract: The invention relates to a composition, its use and a method of its use as a glazing adhesive. The composition comprises an adhesive agent with thermoexpandable microcapsules which act as pressure actuators dispersed therein. The microcapsules are heat triggered so as to release at least one expandable volatile agent encapsulated within the microcapsule shell.

ADHESIVE COMPOSITION COMPRISING THERMOEXPANDABLE MICROCAPSULES

The present invention relates to an adhesive for use in sealing together two surfaces, for use especially in the glazing industry in general and in securing vehicle windscreens and/or windows and/or other vehicle features that may require replacement such as, without limitation, car panels; the invention also provides a method of use for installing and/or replacing vehicle windscreens and/or other fixed glazing on vehicles, buildings or the like.

10 Background of the Invention

Typically to install a window pane in a wooden/plastic/metal frame, the glass pane is firstly held in position against nails or other clasps and then fixed into position by putty or plasters material. Conventional putty is a cement made from whiting and linseed oil which hardens over time to provide a peripheral rim of the window pane, thus separating interior and exterior environments and preventing air, moisture and/or heat transfer. The installation is completed once the putty has dried and this usually takes up to 6 hours or so depending on the kind of plasters used.

20 To remove a window pane after it has been fixed in position in a frame requires the window itself to be shattered so that the hardened putty or plasters can be scraped/chiselled away from the frame. The removal operation can cause damage to the frame and varnishes.

25 In use, the window pane is held rigidly around its edges so that even relatively small vibrational mechanical movements such as with earthquakes or bomb blasts or strong winds can cause the window pane to shatter.

30 In the automotive industry, cars direct from the factory production line typically have the windscreens and other fixed windows, including light assemblies fixed into position by placing the glass against a frame rim and using adhesives so as to direct glaze the glass. The life span of a windscreen and other fixed windows are

significantly shorter than that of the vehicle itself partially due to degradation or damage or being deliberately broken by vandals/car thieves. Thus a motorist may need to replace the windscreen several times during the vehicle's lifetime.

5 Additionally, glued glazings have to be replaced any time the window, especially the windscreen, has been damaged in its optical performance by, for example, impact stones or other fractures or abrasion by wipers. Damage to the window surface can increase the scattering of light and may reduce the visibility to levels below safety limits. Moreover, regulations of motor worthiness (MOT) stipulate that there can be
10 no chips or visual impairments on laminated windscreens, so whereas recent improvements have made the windscreens shatter-proof, they are still prone to chipping and fracturing and thus will require replacement.

15 The process of replacing vehicle windscreens is both laborious and time consuming.
The automotive glass fitter has first to remove the defective windscreen (usually in intact form), however the windscreen is firmly bonded in place and the adhesive sealant is hardened. Typically the fitter uses a device comprising a cheesewire. The cheesewire is used to cut/saw through the hardened rubber along the periphery of the windscreen. This process requires physical force and can lead to musculo-skeletal
20 conditions in the fitters themselves as a result of repetitive strain injury. Further problems associated with this method are that the cheesewires can overheat due to friction, additionally the wires themselves can break.

25 Other methods of detaching the windscreen from the adhesive sealant include: the use of mechanical oscillator knives/cutters to cut through the hardened material or; directed heat such as a laser beam to soften the sealant prior to removing the windscreen with either cheesewire or specialised bladed tools. The problem with a method where heat is directly applied to the sealant is that the heat required to soften the hardened adhesive sealant can concomitantly and inadvertently damage the
30 vehicle's paintwork and/or other exterior surfaces. For example, a pulsed laser that is

set to pulse too fast will not generate enough energy to char the adhesive sealant and a pulsed laser that is set too slow will burn the adhesive sealant and liquify it.

Once the windscreen has been freed from the rubber sealant it can be removed and 5 the surround scraped before it is replaced. It is known from the prior art to use urethane based adhesives to fix/seal the replaced windscreen in place and to apply the adhesive from a dispenser gun to specific peripheral edges so as not to impinge on the viewing capacity of the windscreen. The adhesive typically takes about 8 hours to cure.

10

Recent advances to the industry have provided for the inclusion of fast cure agents/catalysts so as to speed up the time from vehicle drop-off to vehicle collection. The fast cure agents/catalysts can be provided pre-mixed in the adhesive composition or alternatively can be mixed with the adhesive at the point of exit from a dispensing 15 gun. However the problem still remains that the removal of a defective windscreen and its subsequent replacement is a laborious and time consuming process which can result in damage to the dashboard interior or vehicle paint-work.

20 An adhesive that could satisfy vehicle safety crush and crash standards and provide for easy, effective and damage-proof removal of a defective windscreen or other fixed glazing from a vehicle would offer immediate improvement to the industry and consumer.

In a completely different technical field it is known to provide thermoexpandable 25 microcapsules or microspheres for use in the manufacture of porous or lightweight materials with density (weight) reduction, acoustic and thermal insulating properties as covering materials or walls. The microcapsules or microcapsules comprises a polymer shell or shell of some other similar material, the shell being of certain thickness and chemical/physical/mechanical properties. The shell encapsulates 30 materials such as volatile organic solvents, expandable gases or activating agents, including explosives or any other such material which is capable of exploding the

shell and expanding at certain specified conditions with a selected matrix . The microcapsules, when heated to a sufficient temperature, typically in the region of about 75-180 ° C, depending on the encapsulated substance and the shell composition and thickness, can produce an increase of their volume at high expansion rate in 5 some instances at a volumetric expansion limit of up to 70 to 160 times the original volume. The percentage and distribution of the microspheres in a given composition, their expansion ratio, the temperature operating range, the softening transition range of the shell material and the matrix cohesion and consistency are all parameters which are able to influence the expansion volume of a layer between two materials.

10

We have discovered that by mixing an appropriate adhesive in a suitably rheological performance with a certain % in powdered form of specially developed microcapsules having a specific range of size distribution, the resulting composition is effective at providing glazing adhesion and sealing. Moreover, of particular 15 advantage is that the adhesive bonds in the composition can be weakened by the application of direct heat to the composition thereby allowing sufficient softening of the adhesive material so that a vehicle windscreen/fixed glazing can be easily lifted up and so rapidly removed. The lifting pressure can be predicted by a computational software which is part of this invention and treats the expanding microspheres like a 20 spring mechanical pressure actuator in the volume of the adhesive state and like a "bombing" actuator at interfaces between two layers.

We believe that the invention provides the first application/use of a polyester material in the automotive glazing industry.

25

It will be appreciated that the adhesive of the invention has application in other areas especially where two surfaces are to be bonded together and where one surface may subsequently need replacing following damage or ware, for example, and without limitation; shower doors and vehicle panels and other building glazing applications.

30

Reference herein to vehicle is intended to include, without limitation car, lorry, van ship, boat, plane, cable car, helicopter, hovercraft and any other form of transport in which there is fixed glazing.

5 Statement of the Invention

In its broadest aspect the invention provides a composition comprising a heat triggered adhesion-deactivating microcapsule or microsphere or microbead, typically the microcapsule or microsphere or microbead is typically dispersed in another 10 medium such as an adhesive or primer or at an interface between two layers.

According to a first aspect of the invention there is provided a composition comprising an adhesive agent and dispersed therein thermoexpandable microcapsules.

15

Reference herein to microcapsule is intended to include a microsphere or microbead.

Preferably, the microcapsules each comprise a shell which encapsulates at least one expandable gas or volatile expandable agent or an explosive material. Preferably, the 20 shell is composed of a polymer or other suitable material.

Preferably, the adhesive agent is a urethane or polyurethane or polyvinylchloride or a MS polymer.

25 Preferably, the thermoexpandable capsules are microspheres or hollow fibres in the form of a powder of specific range of dimensions and properties.

The powder can be provided with the adhesive agent in a pre-mixed form in a container or the powder can be introduced into and mixed with the adhesive or one 30 component of it at a point of exit from a dispensing device i.e. the composition can be formed as a pre-mix or at the time of, or shortly before, its use. The dispensing

device can be followed by a static mixer suitably lubricated at the point of exit of the composition for optimal blending.

Preferably, the composition additionally comprises a fast cure agent or catalyst,
5 whereby the adhesive composition is rapidly cured or set. Preferably, the composition comprises a colouring agent so that the cured composition is black.

Reference herein to cure is intended to mean the hardening or setting of the adhesive mixture, the hardening or setting can be either chemically or non-chemically
10 enhanced.

Preferably, the microcapsules encapsulate more than one material, ideally the material is selected from the group consisting of an expanding agent, an agent capable of sublimation, water, an explosive material or an activator agent.

15 Preferably, the activator agents are capable of foaming or of shrinkage. The present invention includes the simultaneous use of microcapsules encapsulating a variety of different agents, either separately or in combination. The additional microcapsules are activated by the breaking or permeation of the polymer shell whereby their
20 contents are released so as to interact with the adhesive mix. Their activation is as a result of specified applied conditions and thus is controllable. Microspheres do not break/fracture their shells in the expanding state maintaining their integrity, so that an activated composition comprises intact expanded microspheres and microcapsules which have released their contents into the matrix composition.

25 It will be appreciated that the expanding agent inside the capsule is capable of activating a foaming process of the adhesive composition and that the agent capable of sublimation is to allow the composition to expand under certain specified conditions. Both these processes will occur after the breakage/fracture of the
30 microcapsule shell and thus contribute to facilitating lifting and ease of removing fixed glazing. The inclusion of water in the microcapsules is to allow the adhesive

composition to weaken in certain conditions and the presence of an activator agent is to crosslink or polymerise the adhesive composition whereby shrinkage occurs and the adhesive composition weakens.

5 Preferably, the microsphere's diameter is in the range 10 to 120 μm .

Preferably, the microcapsule shell thickness is in the range 3 to 7 μm .

10 Preferably, the composition comprises microcapsules in the range of 1-30% by volume, and more preferably in the range of 2-10% by volume.

Preferably, the composition is activated by heat wherein the heat activation range is 80-170° C and ideally 120-150° C.

15 Preferably, the composition is composed of a mixture of microcapsules of different diameter or shell thickness or of differing heat activation temperatures or different suitable expanding coefficients.

20 The temperature of a vehicle windscreen can reach over 100°C in natural soak conditions. Thus the heat activation of the microcapsules in the composition of the invention needs to be in excess of any natural temperatures that may occur whilst being below those that could damage a vehicle dashboard trim or paint-work. It is envisaged that the composition of the invention will have application in many fields and many diverse climates hence the composition may be provided with selected heat
25 activation ranges depending on its intended use and/or country of use for both kinds of microcapsule: the expanding microspheres and the microcapsules with breakable shells. For example, in the instance of the composition being used for fixing and sealing a shower door it is envisaged that the adhesive composition microcapsule heat activation range would be in the region of 80-100 °C, whilst for the majority of
30 automotive glazing the microcapsule heat activation range would be in the region of

120-150° C. Optionally in either composition a user may require microcapsules capable of releasing a curing agent and/or an activator agent capable of shrinkage.

Heat activation of the microcapsules causes the beads/fibres to thermoexpand thus
5 creating pressure along the rim of glazing. This in effect reduces the viscosity and the shear or tear stress of the adhesive material. In addition, heat activation or expansion of the microcapsules reduces the cohesive stress and/or interfacial adhesive bonding of the adhesive film between two bonded surfaces, typically the frame and glass layers. The reduction in either cohesive stress and interfacial
10 adhesion, or both together, contribute to reduce failure stress so as to facilitate removal of the glued glazing from the frame once the microcapsules have expanded at the specific temperature range and range of time, typically no more than 5 minutes. The compositions of the present invention thus allows removal of glued glazing by virtue of a reduction in chemical and/or physical bonding of the adhesion at the
15 interface between the adhesive and the two bonded surfaces (glass and frame surfaces). In other words, adhesion failure can only occur at the interface of the two bonded surfaces due to the effect of the expanded microcapsules. In use, and once the microcapsules have been activated the reduction in cohesive forces of the adhesive material and the bonding at interface between material and layers in
20 addition to the expansion of the adhesive material itself, results in the loosening of the whole of the adhesion of the glazing to a frame so that a windscreens or glazing can be easily lifted up and removed therefrom.

According to a further aspect of the invention there is provided use of a composition
25 comprising an adhesive agent and dispersed therein thermoexpandable microcapsules as a glazing adhesive.

Preferably, the composition further includes any one or more of the features herein before described.

According to a yet further aspect of the invention there is provided a composition comprising a primer and dispersed therein thermoexpandable microcapsules.

Preferably, the composition further includes any one or more of the features herein before described.

5

According to a further aspect of the invention there is provided use of a composition comprising a primer and dispersed therein thermoexpandable microcapsules as a glazing adhesive.

10 Preferably, the composition further includes any one or more of the features herein before described.

15 It will be appreciated that the invention also includes the use of microcapsules when applied directly to a glazing face and/or body of a vehicle.

According to a yet further aspect of the invention there is provided a method of installing and/or replacing a vehicle windscreen or fixed glazing comprising the steps of:

- 20 (i) placing a windscreen flush against a window aperture rim of a vehicle,
- (ii) applying the composition of the first aspect of the invention around a peripheral region of the windscreen;
- (iii) allowing sufficient time for the adhesive to cure;
- (iv) applying a heat source to the cured adhesive wherein the heat applied is sufficient to cause thermoexpansion of the microcapsules and thus weaken the adhesive cohesion and interface bonds of the composition; and
- (v) removing the windscreen from the main vehicle body.

25 30 It will be appreciated that in one aspect, the method of installation involves steps i-iii whilst in another aspect the method of replacement involves steps iv-v.

By using the method of the invention as herein described, a vehicle windscreen or fixed glazing can be removed and/or replaced more rapidly and advantageously with less damage to the frame and/or paint work than by prior art methods, thus the method is more cost effective to both the fitter and customer.

5

10

15

20

P32052.2

10

Claims

1. A composition comprising an adhesive agent and dispersed therein thermoexpandable microcapsules.

5

2. A composition according to Claim 1 wherein the microcapsules each comprising a shell, encapsulate at least one expandable gas or volatile expandable agent or an explosive material.

10 3. A composition according to Claim 2 wherein the shell is composed of a polymer.

4. A composition according to any preceding claim wherein the adhesive agent is a urethane or polyurethane or polyvinylchloride or a MS polymer.

15

5. A composition according to any preceding claim wherein the thermoexpandable capsules are microspheres or hollow fibres in the form of a powder.

20 6. A composition according to Claim 5 wherein the powder is provided with the adhesive agent in a pre-mixed form in a container.

7. A composition according to any of Claims 1-5 wherein the composition is formed at the time of, or shortly before, its use.

25

8. A composition according to Claim 7 wherein formation of the composition occurs within a dispensing device or at a point of exit therefrom.

30 9. A composition according to any preceding claim which further includes a fast cure agent or catalyst, whereby the adhesive composition is rapidly cured or set.

10. A composition according to any preceding claim which further includes a colouring agent so that the cured composition is black.
11. A composition according to any preceding claim wherein the microcapsules 5 encapsulate more than one material.
12. A composition according to Claim 11 wherein the additional material is selected from one or more of the group consisting of an expanding agent, an agent capable of sublimation, water, an explosive material or an activator agent.
- 10
13. A composition according to either Claim 11 or 12 wherein the microcapsules encapsulate different agents, either separately or in combination.
14. A composition according to any of claims 11-13 comprising intact expanded 15 microspheres and/or microcapsules which have released their contents into the composition.
- 15
16. A composition according to any preceding claim wherein the microsphere's diameter is in the range 10 to 120 μm .
- 20
17. A composition according to any preceding claim wherein the microcapsules 25 are present in the range of 1-30% by volume
18. A composition according to Claim 17 wherein the microcapsules are present in the range of 2-10% by volume.
- 30
19. A composition according to any preceding claim wherein the composition is activated by heat in a heat activation range of 80-170° C.

20. A composition according to Claim 19 wherein the composition is activated by heat in a heat activation range of 120-150° C.

21. A composition according to any preceding claim comprising a mixture of 5 microcapsules of different diameter or shell thickness or of differing heat activation temperatures or different expanding coefficients.

22. Use of a composition comprising an adhesive agent and dispersed therein thermoexpandable microcapsules for fixing glazing.

10

23. Use of a composition according to Claim 22 wherein the composition further including any one or more of the features recited in Claims 2-21.

24. A composition comprising a primer and dispersed therein thermoexpandable 15 microcapsules.

25. A composition according to Claim 24 further including any one or more of the features of Claims 2-21.

20 26. Use of a composition comprising a primer and dispersed therein thermoexpandable microcapsules as a glazing adhesive.

27. Use of a composition according to Claim 26 including any one or more of the features of Claims 2-21.

25

28. A composition comprising microcapsules for use as a glazing adhesive.

29. A method of installing a vehicle windscreen or fixed glazing comprising the steps of:

30 (i) placing a windscreen flush against a window aperture rim of a vehicle;

- (ii) applying the composition according to any of Claims 1-21 or Claims 24, 25 or 28 around a peripheral area of the windscreens; and
- (iii) allowing sufficient time for the adhesive to cure or primer to dry.

5 30. A method according to Claim 29 wherein prior to application, the composition is blended by a static mixer.

31. A method of removing a vehicle windscreens or fixed glazing comprising the steps of:

- 10 (i) applying a heat source to the cured adhesive wherein the heat applied is sufficient to cause thermoexpansion of the microcapsules and thus weaken the adhesive cohesion and interface bonds of the composition; and
- (ii) removing the windscreens from the main vehicle body.

15

20

25 P32052woclaims

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/GB 00/02059

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09J5/08 C08J9/32 B60J10/02 B60J10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09J C08J B60J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 24441 A (PPG IND ITALIA S R L) 14 September 1995 (1995-09-14) page 4, line 27 -page 5, line 8 example 1 EP 0 717 091 A (NORTON PERFORMANCE PLASTICS CO) 19 June 1996 (1996-06-19) page 2, line 37 - line 55 page 3, line 39 -page 4, line 42 -/-	1-5, 15, 17-20, 24, 25
X		1-5, 9, 11-13, 15, 17-20

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the International filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the International filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the International search report

22 August 2000

31/08/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Schlicke, B

INTERNATIONAL SEARCH REPORT

Int'l. Application No.
PCT/GB 00/02059

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 199248 Derwent Publications Ltd., London, GB; Class A18, AN 1992-394008 XP002145458 & JP 04 292684 A (NIPPON RUBBER CO), 16 October 1992 (1992-10-16) abstract —	1-4, 17-20, 24,25
X	DATABASE WPI Section Ch, Week 199215 Derwent Publications Ltd., London, GB; Class A14, AN 1992-120233 XP002145459 & JP 04 063885 A (ALFA GIKEN KK), 28 February 1992 (1992-02-28) abstract —	1-3,5,9, 10,15, 17,18
X	US 5 064 494 A (DUCK EDWARD W ET AL) 12 November 1991 (1991-11-12) example 1 claim 1 column 1, line 62 -column 2, line 4 —	28
A	EP 0 521 825 A (GURIT ESSEX AG) 7 January 1993 (1993-01-07) abstract —	29-31

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l. Application No	
PCT/GB 00/02059	

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 9524441	A 14-09-1995	IT 1269293 B BR 9507405 A		26-03-1997 07-10-1997
EP 0717091	A 19-06-1996	DE 69517396 D EP 0868492 A WO 9747681 A US 5780523 A		13-07-2000 07-10-1998 18-12-1997 14-07-1998
JP 4292684	A 16-10-1992	NONE		
JP 4063885	A 28-02-1992	JP 3057236 B		26-06-2000
US 5064494	A 12-11-1991	AT 89212 T CA 1304210 A DE 3880976 A WO 8809712 A EP 0318542 A ES 2010290 A JP 1503546 T		15-05-1993 30-06-1992 17-06-1993 15-12-1988 07-06-1989 01-11-1989 30-11-1989
EP 0521825	A 07-01-1993	AT 141222 T AU 1935692 A CA 2073092 A DE 59206897 D ES 2093236 T JP 5201246 A MX 9203907 A ZA 9204911 A		15-08-1996 07-01-1993 04-01-1993 19-09-1996 16-12-1996 10-08-1993 01-01-1993 28-04-1993